# Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. III. The Scope and Mechanisms of Phenyl Alkyl Ketone Reactions[1a]

FRANK E. JUGE, JR.[1b] AND ARTHUR FRY[1c]

*Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701*

*Received January 28, 1969*

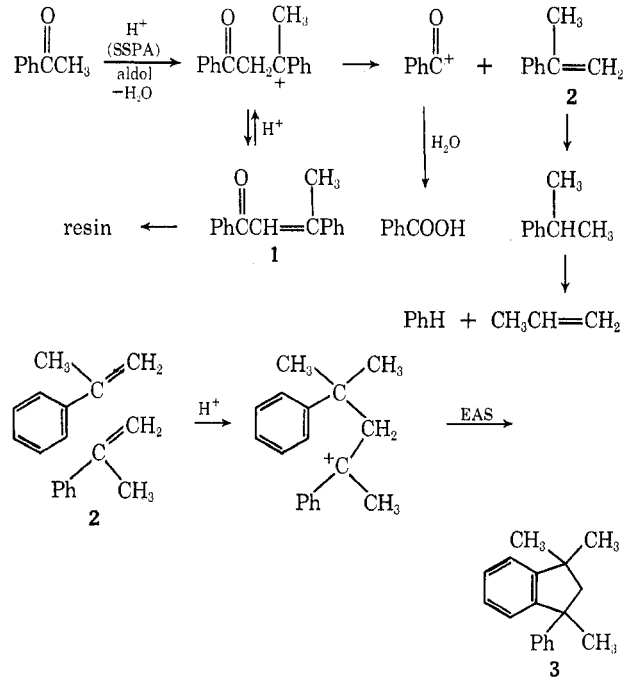
Rearrangement, condensation, disproportionation, and cyclodehydration reactions of phenyl alkyl ketones occur on solid supported phosphoric acid catalyst with good recovery of products. When the alkyl group is methyl or ethyl, disproportionation of aldol condensation products occurs to yield benzoic acid and fragments which eventually yield indans [1,1,3-trimethyl-3-phenylindan (**3**) or 1,1-dimethylindan, respectively]. When the alkyl group is larger than ethyl, functional-group rearrangement followed by cyclodehydration predominates. Butyrophenone and isobutyrophenone produce 1-methylindan in 18 and 43% yields, respectively, and *t*-butyl phenyl ketone gives 2,3-dimethylindene in 31% yield *via* its isomer, 3-methyl-3-phenyl-2-butanone. Significant rearrangement of both straight- and branched-chain alkyl phenyl ketones are observed; however, cyclization reactions seem to predominate in this system. 3-Phenyl-1-propanal cyclized to yield indene, which was reduced to indan (28% yield). Numerous alkenes and alkynes also give indenes and indans in good yields.

Earlier papers in this series[2,3] report the great utility of solid supported phosphoric acid (SSPA) in a flow reactor for catalyzing the rearrangement of aliphatic ketones to isomeric ketones. This research has now been extended to product, scope, and mechanistic studies for a group of phenyl alkyl ketones and related compounds. Rearrangements to isomeric ketones are observed, the primary compounds formed being cyclodehydration (indenes and indans) and disproportionation products from these rearranged ketones.

In previous studies,[4,5] acidic treatment of propiophenone and similar straight-chain aromatic aliphatic ketones gave only decomposition products and resins. Cyclizations of ketones with carbonyl groups $\alpha$ or $\beta$ to the ring have not been observed previously. Branched-chain ketones such as isobutyrophenone[5,6] and pivalophenone[5,7] are known to rearrange to isomeric ketones, but their further cyclization has not been reported. Simons and Ramler[8] studied the reaction of several phenyl alkyl ketones with hydrogen fluoride and found that acetophenone and propiophenone formed benzoic acid and a resin, while isobutyrophenone produced only a resin.

The primary reaction of acetophenone on SSPA catalyst, after seven successive recycles at 360°, is the formation of 1,1,3-trimethyl-3-phenylindan (**3**, 20%) and benzoic acid (30%) (see Table I, run 1). Benzene and small amounts of cumene (9%) and $\alpha$-methylstyrene (**2**, 4%) were also produced. These products could be formed by a disproportionation reaction, according to a reaction path similar to that proposed by Simons and Ramler[8] (Scheme I).[9] For reaction according to this sequence, dypnone (**1**) should give 1,1,3-trimethyl-3-phenylindan (**3**), $\alpha$-methylstyrene (**2**), benzoic acid, cumene, and benzene; $\alpha$-methylstyrene should give **3**, cumene, and benzene; and cumene should give benzene. When these compounds were subjected to the catalyst (Table I, runs 2–4), the expected products were formed; however, probably because of difficulty in forcing the high-melting material through the column rapidly, the major product from dypnone (**1**) was a resin. Perhaps acetophenone, formed from dypnone by a retrograde aldol condensation reaction, could have produced the hydrocarbons and benzoic acid by some other mechanism, but this is unlikely, especially in view of the excellent yield of **3** from $\alpha$-methylstyrene (Table I, run 3).

SCHEME I




The major products of the reactions of propiophenone and related compounds with SSPA catalyst are given in Table I. In an experiment (14 passes over the catalyst, 330°) in which there was a 60% recovery of liquid material, the following compounds were detected: propiophenone, 12%; methyl benzyl ketone, 8%; indan, 3%; 1,1-dimethylindan, 27%; a mixture of 1,2- and 1,3-dimethylindan, 5%; benzoic acid, 2%; ben-

(1) (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of F. E. J. (b) NASA Fellow, 1964–1966. (c) To whom correspondence should be addressed.

(2) W. H. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

(3) A. Fry and W. H. Corkern, *ibid.*, **89**, 5894 (1967).

(4) P. Ramart-Lucas and F. Salmon-Legagneur, *Bull. Soc. Chim. Fr.*, **51** (4), 1069 (1932).

(5) A. E. Favorskii, T. E. Zalesskaya, D. I. Rozanov, and G. V. Chelintzev, *ibid.*, **3** (5), 239 (1936).

(6) A. E. Favorskii and A. A. Chilingaryan, *Compt. Rend.*, **182**, 221 (1926).

(7) T. E. Zalesskaya and T. B. Remizova, *Zh. Obshch. Khim.*, **33**, 3802 (1963).

(8) J. H. Simons and E. O. Ramler, *J. Amer. Chem. Soc.*, **65**, 1390 (1943).

(9) In this and the following formulations the ions are shown as open carbonium ions without specific discussion at this time of the accompanying solvation, counterions, etc.

TABLE I

YIELDS OF THE IMPORTANT PRODUCTS FROM THE MAJOR REACTIONS OF ACETOPHENONE, PROPIOPHENONE, AND RELATED COMPOUNDS WITH SSPA CATALYST

| Run no. | Reactant | Products | No. of passes | Temp, °C | Yield,[a] % |
|---|---|---|---|---|---|
| 1 | Acetophenone | 1,1,3-Trimethyl-3-phenylindan (3) | 7 | 360 | 20 |
| | | Benzoic acid | | | 30 |
| 2 | Dypnone (1) | 1,1,3-Trimethyl-3-phenylindan (3) | 5 | 335 | <1 |
| | | Benzoic acid | | | 10 |
| 3 | α-Methylstyrene (2) | 1,1,3-Trimethyl-3-phenylindan (3) | 5 | 350 | 55 |
| 4 | Cumene | Benzene | 5 | 350 | 16 |
| 5 | Propiophenone | 1,1-Dimethylindan | 14 | 330 | 24 |
| | | Benzoic acid | | | 2 |
| 6 | Methyl benzyl ketone | Indan | 7 | 360 | 4 |
| | | Propiophenone | | | 6 |
| 7 | 1-Phenyl-1-propyne | Propiophenone | 2 | 360 | 19.5 |
| | | Methyl benzyl ketone | | | 5.5 |
| | | Indan | | | 3 |
| 8 | 1-Phenyl-1-propene | *n*-Propylbenzene | 3 | 360 | <1 |
| 9 | Allylbenzene | 1-Phenyl-1-propene | 2 | 360 | 39 |
| 10 | 3-Phenylpropanal | Indan | 2 | 360 | 25 |
| | | Indene | | | 3 |
| 11 | Indene | Indan | 3 | 319 | 49 |

[a] Based on the net amount of ketone reacted and on the stoichiometries in Scheme I or II.

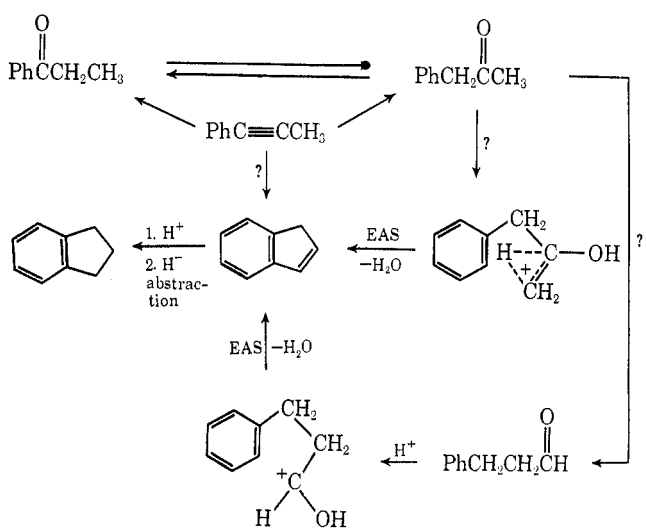
zene, 39%; ethylbenzene, 2%; 1-phenyl-1-propene, 1%; cumene, *n*-propylbenzene, and 1-methylnaphthalene, <1% each.

Neither the rearrangement of propiophenone to methyl benzyl ketone nor the conversion of either ketone into indan had been observed previously, but perhaps the most interesting reaction of propiophenone on SSPA catalyst is disproportionation to benzoic acid and 1,1-dimethylindan, 1,2-dimethylindan, 1,3-dimethylindan, and 1-methylnaphthalene. No path leading to these products involving the self-condensation of propiophenone and reasonable intermediates was evident. The reaction path shown in Scheme II involving an aldol condensation of propiophenone with its rearrangement isomer, methyl benzyl ketone (probably formed by an oxygen-function rearrangement[2,3]), yields the disproportionation products without going through usually high energy intermediates. This sequence is consistent with the observations that methyl benzyl ketone, 1-phenyl-1-propyne, allylbenzene, 3-phenylpropanal, and indene undergo the indicated rearrangement, hydration, reduction, and cyclization reactions (Table I, runs 6–11) and that the cross-aldol condensates of propiophenone with methyl benzyl ketone yield the disproportionation products on the catalyst (1–2.3% yield, not corrected for unreacted condensate) while the self-aldol condensates of each ketone do not.

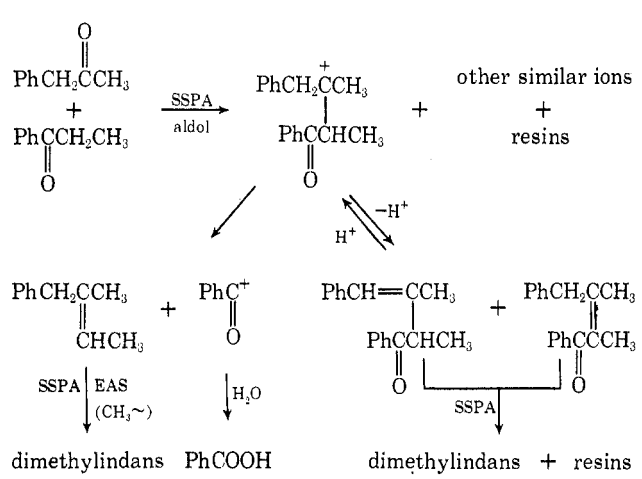
It is interesting to speculate about the mechanism by which an α or β functionally substituted aromatic compound such as propiophenone or methyl benzyl ketone may undergo cyclization at the γ position to a compound such as indene. The ketone rearrangements observed in this work provide a path from the α- to the β-substituted compounds. Further rearrangement to 3-phenylpropanal is unlikely, since aldehydes are known to rearrange to isomeric ketones with considerable facility.[4] Dehydration of methyl benzyl ketone to the nonconjugated 3-phenyl-1-propyne seems un-

SCHEME II

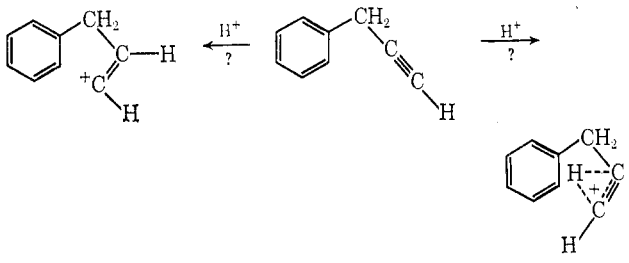
A. Rearrangement and Cyclization




B. Condensation, Disproportionation, and Cyclization

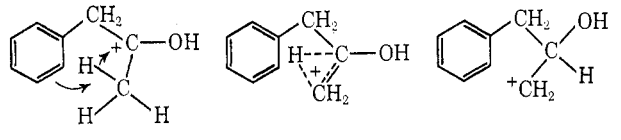


likely in the first place, but cyclization of the protonated, nonconjugated alkyne also seems unattractive, since the linear geometry of the alkyne would need to be altered drastically to permit ring closure. Energetic-



ally, the terminal vinyl cation is also an unattractive possibility.

A more likely cyclization path is the path through the protonated enol of methyl benzyl ketone, as is shown in Scheme II, part A. This protonated enol is seen to occupy an intermediate postion in the "proton-placement energy-barrier" sequence between the ketone conjugate acid and the primary carbonium ion formed by a hydride shift in the conjugate acid.



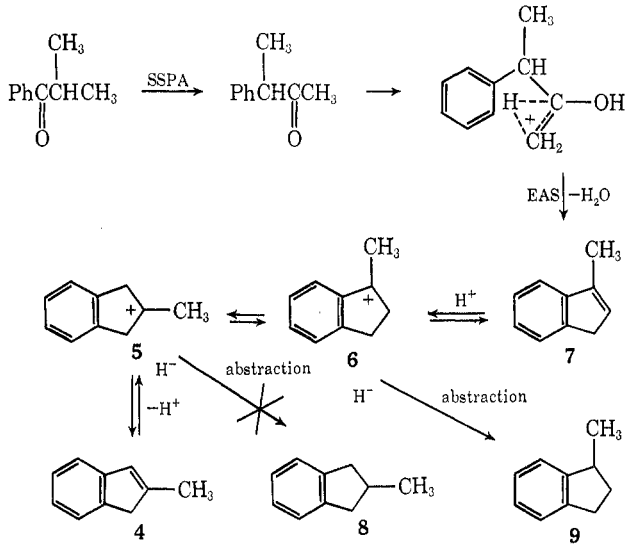
The ketone conjugate acid is undoubtedly formed first, and the terminal carbon atom clearly eventually takes on sufficient positive charge to interact with the ring electrons. Hydrogen, with an electron pair, must be transferred from the terminal carbon atom to the original carbonyl carbon. It is quite probable that the lowest energy path for this sequence of events will have the protonated enol at or near the energy maximum, and this species probably is the immediate precursor to the transition state for the cyclization reaction.

The primary reaction of isobutyrophenone with SSPA catalyst (Table II) (15 passes, 320°, 70% recovery of liquid material) was formation of 1-methylindan (**9**), which made up 59% of the recovered material (43% net yield). The remainder of the recovered material consisted of isobutyrophenone (13%), benzene (15%), 2-methylindene (**4**, 5%), 3-methylindene (**7**, 5%), naphthalene (1%), and 3-phenyl-2-butanone (1%). No cumene, isobutyric acid (from a deacylation), or benzoic acid (from a disproportionation reaction) was detected.

It is evident that cyclization *via* a carbon $\gamma$ to the ring and a reduction step are required to give the major product, which, in this case, is obtained in preparatively useful yields. The simplest view of the reaction is show in Scheme III.

The first step in this sequence is clearly possible, since the rearrangement product, 3-phenyl-2-butanone, is one of the observed products. The amount of the rearranged ketone isolated was greater, 12%, when milder conditions were employed (300°, one pass), than the 1% obtained under more vigorous conditions (320°, 15 passes). The cyclization probably takes place through the protonated enol (see above), and the reduction through carbonium ion formation followed by hydride abstraction from the resinous decomposition

SCHEME III



material deposited on the catalyst [indene forms indan in good yield (Table I, run 11)].

It is interesting to note that no 2-methylindan (**8**) was detected despite a careful search. Thus, in contrast to 3-methylindene (**7**), 2-methylindene (**4**) (which is formed in 5% yield, the same as 3-methylindene) is not reduced to the corresponding indan **8**. It appears that the carbonium ion **5** formed by protonation of 2-methylindene (**4**) deprotonates or rearranges to the more stable conjugated ion **6** much faster than it undergoes the hydride abstraction reaction. The possibility that this reaction might proceed through the alkyne formed by dehydration of 3-phenyl-2-butanone is not particularly attractive, since the linear geometry of the alkyne would have to be altered drastically to permit ring closure (see above). In addition, despite a careful search neither 3-phenyl-1-butyne, nor its expected cyclization product, 1-methylindene, could be detected as reaction products.

The major reaction of butyrophenone (Table II, run 13) is cyclodehydration to the same products as obtained from isobutyrophenone, namely, 1-methylindan (**9**, 32% by glpc analysis of the total recovered liquid product), 3-methylindene (**7**, 8%), 2-methylindene (**4**, 5%), and naphthalene (9%). In addition, benzene (16%), 1-phenyl-2-butanone (5%), traces of butyric acid, and unidentified hydrocarbons (5%) were produced, with 20% of the butyrophenone unreacted. The most likely mechanism for the cyclodehydration would seem to involve oxygen function rearrangement[2,3] of butyrophenone to 1-phenyl-2-butanone and then to 4-phenyl-2-butanone followed by conjugate acid formation and cyclization to 3-methylindene (**7**) followed by reduction to 1-methylindan (**9**). The rearrangement to 1-phenyl-2-butanone was observed, and, when subjected to the catalyst (Table II, run 14), this ketone yields the same products as butyrophenone but in higher yields (7 passes, 21%, *vs.* 20 passes, 18% 1-methylindan). Similarly, when subjected to the catalyst (Table II, run 15), 4-phenyl-2-butanone formed the same products in even higher yields (3 passes, 31% 1-methylindan). In all of these reactions the amount of 3-methylindene relative to the amount of 1-methylindan decreases with each pass. This was

TABLE II

YIELDS OF THE IMPORTANT PRODUCTS FROM THE MAJOR REACTIONS OF ISOBUTYROPHENONE, BUTYROPHENONE, PIVALOPHENONE, AND RELATED COMPOUNDS WITH SSPA CATALYST

| Run no. | Reactant | Products | No. of passes | Temp, °C | Yield, % |
|---|---|---|---|---|---|
| 12 | Isobutyrophenone | 1-Methylindan | 15 | 320 | 43 |
| 13 | Butyrophenone | 1-Methylindan | 20 | 320 | 18 |
| 14 | 1-Phenyl-2-butanone | 1-Methylindan | 7 | 340 | 21 |
| 15 | 4-Phenyl-2-butanone | 1-Methylindan | 3 | 350 | 31 |
| 16 | 1-Phenyl-1-butyne | Butyrophenone | 3 | 360 | 18 |
| | | 1-Phenyl-2-butanone | | | 3 |
| 17 | 4-Phenyl-1-butyne | 1-Methylindan | 2 | 360 | 32 |
| 18 | 4-Phenyl-1-butene | 1-Methylindan | 7 | 345 | 66 |
| 19 | 1-Phenyl-2-butene | 1-Methylindan | 2 | 360 | 79 |
| 20 | Pivalophenone | 2,3-Dimethylindene | 5 | 360 | 35[a] |
| | | 1,2-Dimethylindan | | | 17[a] |
| 21 | 3-Methyl-3-phenyl-2-butanone | 2,3-Dimethylindene | 8 | 360 | 31[a] |
| | | 1,2-Dimethylindan | | | 11 |

[a] Not corrected for recovered 3-methyl-3-phenyl-2-butanone.

especially noticeable with 4-phenyl-2-butanone, where the ratio of 3-methylindene to 1-methylindan went from 1.4 after the first pass to 0.23 after the third pass. These data support a mechanism involving ketone intermediates.

The yield (43%) of 1-methylindan from isobutyrophenone is higher than the yield (18%) from butyrophenone under comparable conditions (Table II, runs 12 and 13), even though the cyclization step would appear to involve a lower energy intermediate (the conjugate acid) in the butyrophenone case. Perhaps the ketone rearrangement steps are partially rate limiting, and the branched-chain compound reacts faster, or perhaps the methyl group of the ketone conjugate acid interferes sterically with the electrophilic attack on the ring.

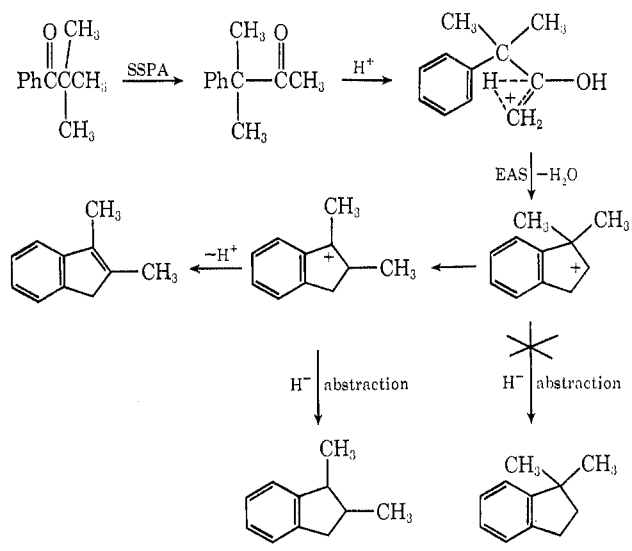
The possibility that the main cyclization mechanism for butyrophenone might involve alkyne intermediates was investigated (Table II, runs 16 and 17). After one pass over the SSPA catalyst, 1-phenyl-1-butyne was 75% converted into a mixture of butyrophenone and 1-phenyl-2-butanone, with only traces of 1-methylindan and 3-methylindene present. After three passes, most of the alkyne was gone, the main products were the two ketones, and the concentrations of 1-methylindan and 2-and 3-methylindene were beginning to build up. When 4-phenyl-1-butyne was subjected to the catalyst (Table II, run 17), the cyclization products were formed in good yield, and no ketones were detected. In both runs 16 and 17 the products could have been formed from the alkynes directly or from ketones produced by the hydration of the alkynes. It should be noted that the protonated form of 4-phenyl-1-butyne does not suffer from the geometrical cyclization difficulty mentioned above for other alkynes.

When 4-phenyl-1-butene and 1-phenyl-2-butene were subjected to the catalyst (Table II, runs 18 and 19), both formed 1-methylindan in excellent yield. However, no indenes were formed, ruling out unique paths involving alkene intermediates in the ketone and alkyne cyclizations.

When pivalophenone was subjected to the SSPA catalyst (Table II, run 20), extensive rearrangement to its isomer, 3-methyl-3-phenyl-2-butanone, occurred after one pass, but the expected cyclodehydration product from the isomeric ketone (1,1-dimethylindan) was not formed. Instead, a mixture (73% recovery of liquid material) containing 2,3-dimethylindene (46%) 1,2-dimethylindan (23%), 1-methylnaphthalene (3%) 1-methylindan (6%), and 13% of an unresolved mixture of 3-methyl-3-phenyl-2-butanone and 2-methylnaphthalene was obtained, 3-Methyl-3-phenyl-2-butanone was subjected to the SSPA catalyst (Table II, run 21) and gave the same products in approximately the same yields as pivalophenone.

It seems evident that pivalophenone first rearranges to 3-methyl-3-phenyl-2-butanone, which then cyclizes, as in Scheme IV. The isomerization of pivalophenone

SCHEME IV




to 3-methyl-3-phenyl-2-butanone is reported[10] to be 98% complete in 25 hr at room temperature with perchloric acid, demonstrating the ease with which this ketone rearranges.

Solid supported phosphoric acid catalyst has been shown to be an excellent medium for aliphatic ketone rearrangements.[2] However, results of the present research show that with phenyl alkyl ketones, rearrangement is followed by secondary reactions (disproportion-

(10) T. B. Remizova and T. E. Zalesskaya, *Zh. Obshch. Khim.*, **34**, 1395 (1964).

ation or cyclodehydration) which destroy the rearrangement isomer which is produced. When the alkyl moiety is larger than ethyl (*n*-propyl, isopropyl, *t*-butyl), rearrangement followed by cyclization to a methyl or dimethyl substituted indene predominates over condensation and disproportionation. The indenes which are thus produced are protonated and the carbonium ions formed abstract hydride ions (probably from polymeric material which builds up on the catalyst) to produce indans in good yield.

This catalyst seems to be an excellent medium for cyclizations. It has long been recognized[11,12] that most phenyl-substituted ketones and olefins polymerize (except for those giving a tertiary carbonium ion at the 3 position) before cyclizing in acid media. In addition, indenes, once formed, polymerize in most acid media.[13] However, on SSPA catalyst, cyclizations with good yields were observed even with compounds such as 1-phenyl-1-propyne, methyl benzyl ketone, 3-phenyl-1-propanal, and numerous phenyl-substituted butanones, butynes, and butenes which would polymerize in other acid media.

In many cases, treatment of the appropriately substituted olefins with SSPA catalyst appears to be the method of choice for the preparation of substituted indans.

## Experimental Section

**General Experimental Technique and Instrumentation.**[14]—A complete description of catalyst preparation, reactor, and recovery systems and gas chromatographs used in this study has been given in a previous paper of this series.[2] The weight ratio of 85% phosphoric acid to support (Chromosorb W, Johns-Manville) ranged from 4.5:1 to 6:1 with little difference in catalyst activity noted. A flow rate of 65 ml/hr of reactant over a bed of *ca.* 90 g of catalyst was used, with a nitrogen carrier flow rate of 5–10 ml/min (mean residence time *ca.* 10–20 min).

The weight percentage values for the various products were calculated by glpc analysis using *n*-propylbenzene as an internal standard according to the technique of Lo Chang and Karr.[15] The chemical yields were then calculated from these weight percentage values, the total weight of the liquid sample being analyzed (corrected for nonvolatile residues which were not included in the glpc analyses), and the stoichiometries of Schemes I–IV. For separable solid compounds, *e.g.*, benzoic acid, the weights were measured directly.

**Reactions of Acetophenone and Related Compounds.**—Acetophenone (50 ml) was passed seven times over the catalyst at 360 ± 5°. The 30 ml of liquid product recovered was washed with ammonium hydroxide, and 6.0 g of benzoic acid was recovered from the basic extract. The organic layer was dried, filtered, and distilled. Six fractions were collected and 7.1 g of residue remained in the kettle. Fraction 1, bp 65–80° (735 mm), 5.0 g, was essentially pure benzene. Fraction 2, bp 80–120° (735 mm), 2.1 g, contained cumene and α-methylstyrene, which were separated by preparative glpc on a QF-1 column and identified by their spectra. Fractions 3 and 4 were mainly unreacted acetophenone. Fraction 5, bp 134–140° (10 mm), 1.2 g, was essentially pure 1,1,3-trimethyl-3-phenylindan (**3**): mp 51–52°; $n^{25}$D 1.5682 [lit.[16] mp 52–53°; bp 155° (12 mm); $n^{20}$D 1.56809]; ir ($CCl_4$) 1380 $cm^{-1}$ (geminal dimethyl); nmr $\delta_{TMS}^{CCl_4}$ 1.01 (s, 3 H, $CCH_3$), 1.30 (s, 3 H, $CCH_3$), 1.63 (s, 3 H, $CCH_3$), 2.15 (d, 1 H, CH), 2.41 [d, 1 H, CH, $J_{AB/(B-A)}$ = 0.33 Hz (indicating[17] protons on the same carbon but in different environments, theoretical value 0.37], and 7.03 and 7.07 (two overlapping singlets, 9 H ($C_6H_4$ and $C_6H_5$). The ir and nmr spectra of compound **3** are identical with those of 1,1,3-trimethyl-3-phenylindan prepared by subjecting α-methylstyrene to the catalyst. Dypnone, α-methylstyrene, and cumene were subjected to the catalyst and the products were separated and identified in the same manner as described for acetophenone.

**Reactions of Propiophenone and Related Compounds.**—The commercial propiophenone used was first purified by preparative glpc. A 50-ml sample of the ketone was passed over the catalyst 14 times at 330° with a recovery of 30 ml of liquid. The product was worked up and distilled, and the components were separated by glpc on SE-30 and QF-1 preparative columns. Benzene, ethylbenzene, cumene, *n*-propylbenzene, indan, 1-phenyl-1-propene, and methyl benzyl ketone were isolated and identified by comparison of their ir and nmr spectra and glpc retention times on several different columns with those of authentic samples. A component of the fraction with a boiling point of 58–74° (10 mm), 7.91 g, was isolated on a QF-1 column at 150°, giving 2.2 ml of pure 1,1-dimethylindan: $n^{20}$D 1.5140 (lit.[18] $n^{20}$D 1.5141); ir (neat) 1376 and 1355 $cm^{-1}$ (geminal dimethyl); nmr $\delta_{TMS}^{CCl_4}$ 1.20 [s, 6 H, $C(CH_3)_2$], 1.83 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.82 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), and 6.98 (s, 4 H, $C_6H_4$); mass spectrum (70 eV) *m/e* (rel intensity) 146 (14.7), 131 (100), 116 (7.7), 115 (14.4), 91 (19.3), 77 (7.6), 51 (8.6), and 39 (8.9). A mixture of 1,2- and 1,3-dimethylindan was obtained by preparative glpc (SE-30 column). All of the major infrared peaks of both indans match those for the two pure indans.[19] The nmr spectrum indicates that both dimethylindans are present: $\delta_{TMS}^{CCl_4}$ 1.16 (d, 3 H, $CHCH_3$, 2-methyl of 1,2-dimethylindan) 1.25 (d, 3 H, $CHCH_3$, 1-methyl of 1,2-dimethylindan), 1.28 (d, 6 H, $CHCH_3$, 1- and 3-methyls of 1,3-dimethylindan), 1.5–3.2 (m, $CH_3CH$ and $CH_2$), 6.97 (s, 4 H, $C_6H_4$), and 7.01 (s, 4 H, $C_6H_4$). A positive Jones oxidation of the mixture indicates the presence of benzylic hydrogens. Further separation of this mixture by preparative glpc gave nearly pure 1,2-dimethylindan (determined by ir and nmr spectra). 1-Methylnaphthalene, still somewhat impure, was obtained by preparative glpc.

Methyl benzyl ketone, 3-phenylpropanal, 1-phenyl-1-propene, allylbenzene, and indene were treated with the catalyst and their products were separated by glpc and analyzed in the same manner as described above.

Aldol condensates of propiophenone, of methyl benzyl ketone, and of a 2.7:1 molar mixture of propiophenone with methyl benzyl ketone were prepared[14] using gaseous HBr. The three condensates (30 g) were mixed with equal volumes of benzene, and 1 ml of water and passed over the catalyst six times. A sample (0.005 ml) of the reaction mixture was analyzed by glpc after each pass.[14] Benzoic acid was extracted after the last pass with 20% $NH_4OH$ and precipitated with dilute HCl.

**Identification of Isobutyrophenone, Butyrophenone, and Pivalophenone Reaction Products.**—Isobutyrophenone, butyrophenone, pivalophenone, and related compounds were passed over the catalyst, and the reaction mixtures were worked up and analyzed in the usual way.

Benzene, naphthalene, and 3-phenyl-2-butanone were isolated in pure form from the recovered isobutyrophenone reaction mixture and identified by their ir and nmr spectra. A distillation fraction, bp 67–68° (10 mm), contained 1-methylindan, which was purified by glpc: $n^{25}$D 1.5145 [lit.[19] bp 60–70° (12 mm); $n^{25}$D 1.5241]; nmr $\delta_{TSM}^{CCl_4}$ 1.19 (d, 3 H, $CHCH_3$), 1.60 (m, 1 H, CHH), 2.12 (m, 1 H, CHH), 2.60–3.28 (m, 3 H, $CH_2$ + $CHCH_3$), and 6.98 (s, 4 H, $C_6H_4$); ir and uv spectra identical with those of 1-methylindan;[19] mass spectrum (70 eV) *m/e* (rel intensity) 132 (31), 131 (30.7), 130 (20.5), 117 (100), 91 (18.1), 77 (10.9), and 63 (13.6). 3-Methylindene was separated by glpc from a fraction with a boiling point of 68–88° (10 mm) [lit.[20] bp 70° (10 mm)]; nmr $\delta_{TMS}^{CCl_4}$ 2.12 [s (fine splitting), 3 H, $C{=}CCH_3$], 3.20 [s (fine splitting), 2 H, $CH_2$], 6.04 [s (fine splitting), 1 H, C=CH], and 6.95–7.2 (m, 4 H, $C_6H_4$); ir spectrum identical with that of 3-methylindene;[21] mass spectrum (70 eV) *m/e* (rel

(11) M. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).
(12) W. von Miller and G. Rhode, *Chem. Ber.*, **23**, 1881 (1890).
(13) C. Bradsher, *Chem. Rev.*, **38**, 447 (1946).
(14) See F. E. Juge, Jr., Ph.D. Dissertation, University of Arkansas, 1967, for full experimental details.
(15) Lo Chang and C. Karr, Jr., *Anal. Chim. Acta*, **21**, 474 (1959).
(16) E. Bergman, H. Taubadel, and H. Weiss, *Chem. Ber.*, **64**, 1493 (1932).
(17) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 3rd ed, The Macmillan Co., Inc., New York, N. Y., 1963, p 90.
(18) J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961).
(19) J. Entel, C. H. Ruof, and H. C. Howard, *Anal. Chem.*, **25**, 1303 (1953).
(20) E. Rodd, "Chemistry of Carbon Containing Compounds; A Modern Treatise," Vol. 12A, Elsevier Publishing Co., Amsterdam, 1962, p 107.
(21) American Petroleum Institute, "Catalog of Infrared Spectral Data," Serial No. 1598, Project No. 44, Carnegie Institute of Technology, Pittsburg, Pa.

intensity) 130 (100), 129 (64.9), 138 (36.6), 127 (17.6), 115 (97.5), 77 (15.4), 65 (12.7), 63 (21.8), 51 (29.3), and 39 (20.9). 2-Methylindene was isolated by glpc from the same fraction [lit.[20] bp 79° (10 mm)]: nmr $\delta_{TMS}^{CCl_4}$ 2.10 [s (fine splitting), 3 H, C=CCH$_3$], 3.17 (s, 2 H, CH$_2$), 6.36 [s (fine splitting), 1 H, C=CH], and 6.9–7.2 (m, 4 H, C$_6$H$_4$); ir spectrum identical with that of 2-methylindene.[22] The mass spectrum shows nearly the same cracking pattern as 3-methylindene and the mass spectra of both indenes are similar to that of a mixture of methylindenes found in the literature.[23] These same products were isolated and identified from the SSPA reactions of butyrophenone, 1-phenyl-2-butanone, 4-phenyl-2-butanone, 1-phenyl-1-butyne, and 4-phenyl-1-butyne. 1-Methylindan was isolated and identified similarly from the SSPA reactions of 4-phenyl-1-butene and 1-phenyl-2-butene.

Pivalophenone was prepared by a reverse Grignard reaction[24] and subjected to the catalyst in the same manner as described previously. Benzene, 1-methylindan, and 1,2-dimethylindan were isolated by preparative glpc and identified by comparison of their ir and nmr spectra and glpc retention times with those of authentic samples. 1- and 2-methylnaphthalene were isolated as a 1:1 mixture and identified by comparison of their physical and spectral properties with those of an authentic 1:1 mixture. A distillation fraction, bp 110–125° (30 mm), yielded 3.87 g of 2,3-dimethylindene by preparative glpc: mp 9–10° (lit.[25] mp 11°); ir spectrum identical with that for 2,3-dimethylindene;[22] nmr $\delta_{TMS}^{CCl_4}$ 1.75 (s, 6 H, CH$_3$C=CCH$_3$), 2.81 (br s, 2 H, CH$_2$), and 7.05 [s (fine splitting), 4 H, C$_6$H$_4$].

3-Methyl-2-butanone was allowed to react with the catalyst, and the 2,3-dimethylindene product, obtained by preparative glpc, was dissolved in benzene and subjected to fresh catalyst. The products were analyzed by glpc and nmr, showing 28% conversion of the indene into the same products obtained from pivalophenone and 3-methyl-3-phenyl-2-butanone.

**Registry No.**—**3**, 3910-35-8; **4**, 2177-47-1; **7**, 767-60-2; **9**, 767-58-5; 1,1-dimethylindan, 4912-92-9; 2,3-dimethylindene, 4773-82-4.

(22) T. L. Yarboro, C. Karr, Jr., and P. A. Estep, *J. Chem. Eng. Data*, **6**, 421 (1961).

(23) American Petroleum Institute, "Catalog of Mass Spectral Data," Serial No. 1250, Project No. 44, Carnegie Institute of Technology, Pittsburg, Pa.

(24) J. Ford, C. Thompson, and C. Marvel, *J. Amer. Chem. Soc.*, **57**, 2619 (1935).

(25) G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publishing Corp., New York, N. Y., 1947, p 48.

# The Reduction–Methylation of Derivatives of 3-Buten-2-one[1a]

LAWRENCE E. HIGHTOWER,[1b] LOWRIE R. GLASGOW,[1b] KEARFOTT M. STONE,[1b] DAVID A. ALBERTSON,[1b] AND HOMER A. SMITH

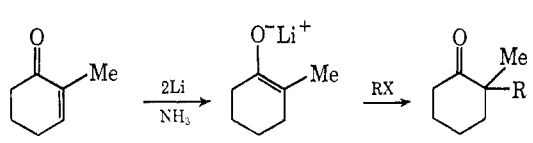
*Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, Virginia 23943*

*Received July 25, 1969*

The lithium–liquid ammonia reduction and reduction–methylation of 3-buten-2-one derivatives *trans*-4-phenyl-3-buten-2-one (**1a**), 3-methyl-4-phenyl-3-buten-2-one (**1b**), and 4-methyl-3-penten-2-one (**1c**) have been investigated. In each case the only monomethylation product obtained was derived from the specific lithium enolate generated reductively. Unlike 2-cyclohexenone derivatives, open-chain enones **1a–1c** also gave much polymethylation, ascribed to the effect of the conjugate base of the proton donor employed in the reduction step. Polymethylation was minimized by the use of triphenylmethanol as proton donor or by the addition of excess acetone with the alkylating agent.

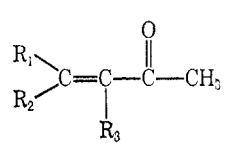
Stork and coworkers[2] have developed a procedure for the reduction–alkylation of an $\alpha,\beta$-unsaturated ketone to give the $\alpha$-alkyl saturated ketone uncontaminated with the $\alpha'$-alkyl isomer. The procedure consists of treatment of an $\alpha,\beta$-unsaturated ketone with 2 equiv of lithium in liquid ammonia to produce a specific lithium enolate, followed by treatment of the enolate with an alkyl halide in an appropriate solvent, as shown for 2-methyl-2-cyclohexenone in Scheme I.

SCHEME I

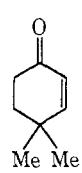



The specificity of the reduction–alkylation depends upon the relatively slow equilibration among structurally isomeric lithium enolates[2–6] and has been confirmed in several studies on reduction–alkylation in cyclic systems.[7–9]

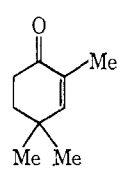
Side reactions leading to polyalkylation products are generally moderate in extent for the reduction–alkylation of derivatives of 2-cyclohexenone[2,9] but extensive for systems in which the enone moiety is not part of a ring. In the present study, the reduction–methylation of some 3-buten-2-one derivatives (**1a–1c**) has been carried out with a view toward investigating the reaction pathway by which polymethylation occurs and finding optimum conditions for monomethylation. Some further work on cyclic systems has been carried out with 4,4-dimethyl-2-cyclohexenone (**1d**) and 2,4,4-trimethyl-2-cyclohexenone (**1e**).




**1a**, $R_1$ = Ph; $R_2$ = $R_3$ = H
**b**, $R_1$ = Ph; $R_2$ = H; $R_3$ = Me
**c**, $R_1$ = $R_2$ = Me; $R_3$ = H




**1d**




**1e**

(1) (a) Supported by the National Science Foundation and the Research Corporation. (b) Undergraduate Research Participant, National Science Foundation.

(2) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, **87**, 275 (1965).

(3) (a) R. E. Schaub and M. J. Weiss, *Chem. Ind.* (London), 2003 (1961); (b) R. Deghenghi and R. Gaudry, *Tetrahedron Lett.*, 489 (1962); (c) M. J. Weiss, R. E. Schaub, J. F. Poletto, G. R. Allen, Jr., and C. J. Coscia, *Chem. Ind.* (London), 118 (1963); (d) R. Dehgenghi, C. Revesz, and R. Gandry, *J. Med. Chem.*, **6**, 301 (1963); (e) M. J. Weiss, R. E. Schaub, G. R. Allen, Jr., J. F. Poletto, C. Pidacks, R. B. Conrow, and C. J. Coscia, *Tetrahedron*, **20**, 357 (1964); (f) H. O. House and T. M. Bare, *J. Org. Chem.*, **33**, 943 (1968).

(4) D. Caine, *ibid.*, **29**, 1868 (1964).

(5) H. O. House and B. M. Trost, *ibid.*, **30**, 2502 (1965).

(6) H. O. House, B. A. Tefertiller, and H. D. Olmstead, *ibid.*, **33**, 935 (1968).

(7) D. Caine and B. J. L. Juff, *Tetrahedron Lett.*, 4695 (1966).

(8) D. Caine and B. J. L. Huff, *ibid.*, 3399 (1967).

(9) H. A. Smith, B. J. L. Huff, W. J. Powers, and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967).